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## The Crystal and Molecular Structure of $\mu$ -1,2,3,4,5,6,7,8-Octaethylporphinatobis[dicarbonylrhodium(I)]

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The title compound crystallizes in the monoclinic system, space group  $P2_1/c$ , with  $a=8.778$  (2),  $b=12.145$  (2),  $c=19.134$  (3) Å,  $\beta=108.94$  (2)° and  $Z=2$ . The crystal structure was solved by the heavy-atom method and refined by the least-squares method, the final conventional  $R$  value being 0.060 for 2343 non-zero reflexions. The metalloporphyrin is centrosymmetric; two Rh(I) atoms are bonded to the porphyrin, one above and the other below the macrocyclic plane. Each Rh atom is coordinated in a square-planar arrangement by two adjacent pyrrole nitrogen and two carbonyl carbon atoms (Rh–N 2.084 and Rh–C 1.85 Å, average) and deviates by 0.105 Å from the basal plane of these four atoms toward the mid-point of the other two nitrogen atoms. The porphinato skeleton is so deformed that the pyrrole rings take an envelope conformation at N and the adjacent ring planes make an angle of 18.3°.

### Introduction

Several X-ray investigations of common metalloporphyrins have revealed that the dimensions of the porphyrins change with the covalent radii of the metals and the porphinato skeletons are slightly ruffled.\* The metals examined have been in the divalent or higher oxidation state (Hoard, 1971; Collins, Scheidt & Hoard, 1971). Little work on the monovalent metalloporphyrins has been reported but it has been suggested that the metals are above and below the macrocyclic plane (Falk, 1964). Recent X-ray analysis of the rhenium(I) complex of  $\alpha,\beta,\gamma,\delta$ -tetraphenylporphine has shown that the two metals bind to the macrocycle one on each side, each metal being coordinated octahedrally by the three nitrogen atoms of the porphyrin and the three carbonyl molecules. Consequently the two pyrrole rings which are situated on the diagonal through the centre are directed upwards and downwards (Cullen, Meyer, Srivastava & Tsutsui, 1972).

On the incorporation of the metal with the porphyrin *in vitro*, the reaction kinetics favour a displacement rather than a dissociation mechanism (Phillips, 1963; Falk, 1964). At an intermediate stage, the interaction of porphyrin with the metal would be maximized by deforming the macrocycle. The deformability of the porphyrin skeleton is, therefore, a stereochemical basis for the mechanism and it is interesting to examine whether or not there are different modes of deformation of porphyrins.

Crystallographic studies have been performed on the analogues containing rhodium(I) with square-planar

coordination. In the present paper we describe the detailed crystal and molecular structure of  $\mu$ -1,2,3,4,5,6,7,8-octaethylporphinatobis[dicarbonylrhodium(I)]. A preliminary account has already been reported (Takenaka, Sasada, Omura, Ogoshi & Yoshida, 1973).

### Experimental

The title metalloporphyrin was prepared by three of the authors (Z.Y., H.O. & T.O.)\* The dark-brown needles were recrystallized from a chloroform–benzene solution by slow evaporation to dryness. The unit-cell dimensions were determined by least-squares calculations from zero-layer Weissenberg photographs taken with Cu  $K\alpha$  radiation about the  $a$  and  $b$  axes, calibration being made with superposed Si lines [ $a(\text{Si})=5.43075$  Å at 25°C]. The density was measured by flotation in an aqueous solution of potassium iodide. The crystal data are summarized in Table 1. Since there are two formula units per cell, the molecule should be centrosymmetric.

The reflexion data were collected with Cu  $K\alpha$  radiation on equi-inclination Weissenberg photographs for

\* This compound was prepared by the method used for (oep)[Rh<sub>2</sub>(CO)<sub>4</sub>Cl]H (oep = 1,2,3,4,5,6,7,8-octaethylporphinato) (Yoshida, Ogoshi, Omura, Watanabe & Kurosaki, 1972). In the present study, it was found that (oep)[Rh<sub>2</sub>(CO)<sub>4</sub>Cl]H shows a strong tendency to liberate HCl in organic solvents.

Table 1. Crystal data

C <sub>40</sub> H <sub>44</sub> N <sub>4</sub> O <sub>4</sub> Rh	
F.W. 850.6	
$a = 8.778 \pm 0.002$ Å	Space group: $P2_1/c$
$b = 12.145 \pm 0.002$	Systematic absences:
$c = 19.134 \pm 0.003$	$0k0, k \neq 2n; h0l, l \neq 2n$
$\beta = 108.94 \pm 0.02^\circ$	$D_m = 1.462 \text{ g cm}^{-3}$
$U = 1929.4 \pm 0.5 \text{ \AA}^3$	$D_x = 1.462 \text{ g cm}^{-3}$
$\mu(\text{Cu } K\alpha) = 76.8 \text{ cm}^{-1}$	$Z = 2$

\* The skeletons of the mono- and di-cationic porphyrins are deformed markedly by repulsion between the inner hydrogen atoms (Hirayama, Takenaka, Sasada, Watanabe, Ogoshi & Yoshida, 1974a, b; Stone & Fleischer, 1968).

layers 0–6 about the  $a$  axis and for layers 0–8 about the  $b$  axis. Photographs about the former axis were integrated but those about the latter were not. Four crystals were used for the  $a$  axis rotation to prevent degradation. Their dimensions were  $0.10 \times 0.13 \times 0.50$  mm for layers 0 and 1,  $0.15 \times 0.15 \times 0.60$  mm for 2,  $0.14 \times 0.15 \times 0.60$  mm for 3, and  $0.07 \times 0.20 \times 0.46$  mm for 4, 5 and 6. For the  $b$  axis rotation, only one crystal of dimensions  $0.10 \times 0.15 \times 0.30$  mm was used.

The intensities were measured by TV densitometer (Izumi, 1971; Shimanouchi, Ibata & Sasada, 1971), and were corrected for Lorentz and polarization effects and for spot size (Takenaka & Sasada, 1973), but not for absorption. Two series of relative intensities were then cross-correlated and placed on an absolute scale by the Wilson (1942) method. The number of independent reflexions thus obtained was 3980, of which non-zero reflexions numbered 2845.

### Structure determination

The structure was solved by the heavy-atom method. The atomic coordinates and thermal parameters, first

isotropic and then anisotropic, were refined by the least-squares method using a block-diagonal matrix approximation; the quantity minimized was  $\sum w\Delta^2$  ( $\Delta = |F_o| - |F_c|$ ). Of 2845 non-zero reflexions, 2343 reflexions which were obtained from the integrated photographs were used for refinement. 16 hydrogen atoms, not including those attached to the two methyl carbon atoms C(12) and C(18), were identified on a difference map, after the conventional  $R$  value reached 0.063. In further refinements, however, the hydrogen coordinates derived from a suitable geometry were not refined. The following weights were applied:

$$w = \exp[-(as^2 + bt^2 + cst + ds + et + f)],$$

where  $s = |F_o| \times 10^{-2}$  and  $t = \sin \theta/\lambda$  for  $|F_o| \geq 9.98$

and  $w = 1/\langle \Delta^2 \rangle$ , for  $|F_o| < 9.98$ .

The coefficients  $a$ ,  $b$ ,  $c$ ,  $d$ ,  $e$  and  $f$  were evaluated by least-squares calculations so that the distribution of  $w\Delta^2$  in  $(s, t)$  space was made as uniform as possible; their values in the final stage of refinement were 1.590, 21.01, 12.79,  $-2.692$ ,  $-24.65$  and 6.890, respectively. The least-squares refinement of the structure

Table 2. The final atomic coordinates and thermal parameters

The anisotropic temperature factor is of the form  $\exp(-h^2\beta_{11} - k^2\beta_{22} - l^2\beta_{33} - hk\beta_{12} - hl\beta_{13} - kl\beta_{23})$ . Estimated standard deviations in the least significant digits are in parentheses.

	$x/a$	$y/b$	$z/c$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Rh	0.15818 (7)	0.04378 (4)	0.05604 (2)	0.0137 (1)	0.00667 (3)	0.00302 (1)	0.0015 (1)	0.00705 (5)	0.00016 (4)
N(1)	0.1365 (8)	0.0954 (5)	0.0504 (3)	0.014 (1)	0.0068 (4)	0.0032 (2)	0.0071 (7)	0.0011 (4)	0.0011 (4)
N(2)	0.1963 (8)	0.1120 (4)	0.0186 (3)	0.009 (1)	0.0066 (4)	0.0037 (2)	0.0025 (9)	0.0087 (6)	0.0004 (4)
C(1)	0.068 (1)	0.1874 (6)	0.0880 (4)	0.017 (2)	0.0071 (5)	0.0042 (2)	0.002 (1)	0.011 (1)	0.0018 (5)
C(2)	0.149 (1)	0.2152 (7)	0.1403 (5)	0.019 (2)	0.0090 (6)	0.0042 (3)	0.000 (2)	0.010 (1)	0.0034 (6)
C(3)	0.262 (1)	0.1364 (7)	0.1358 (4)	0.017 (2)	0.0086 (5)	0.0038 (2)	0.000 (1)	0.0099 (9)	0.0012 (6)
C(4)	0.252 (1)	0.0594 (6)	0.0794 (4)	0.011 (1)	0.0083 (5)	0.0034 (2)	0.003 (1)	0.0078 (8)	0.0011 (5)
C(5)	0.340 (1)	0.0382 (6)	0.0609 (4)	0.015 (2)	0.0079 (4)	0.0031 (2)	0.002 (1)	0.0040 (8)	0.0002 (6)
C(6)	0.3045 (9)	0.1210 (5)	0.0177 (4)	0.011 (1)	0.0067 (4)	0.0033 (2)	0.004 (1)	0.0054 (7)	0.0003 (5)
C(7)	0.367 (1)	0.2330 (6)	0.0096 (4)	0.015 (2)	0.0072 (5)	0.0041 (2)	0.006 (1)	0.0075 (9)	0.0001 (5)
C(8)	0.288 (1)	0.2891 (6)	0.0297 (5)	0.016 (2)	0.0071 (5)	0.0051 (3)	0.008 (1)	0.009 (1)	0.0021 (6)
C(9)	0.178 (1)	0.2136 (5)	0.0461 (4)	0.021 (2)	0.0056 (4)	0.0042 (2)	0.006 (1)	0.010 (1)	0.0018 (5)
C(10)	0.064 (1)	0.2434 (6)	0.0812 (5)	0.022 (2)	0.0072 (5)	0.0048 (3)	0.003 (1)	0.014 (1)	0.0024 (6)
C(11)	0.105 (1)	0.3097 (8)	0.1932 (6)	0.026 (2)	0.0110 (8)	0.0057 (4)	0.005 (2)	0.015 (1)	0.0073 (9)
C(12)	0.031 (2)	0.288 (1)	0.2580 (8)	0.037 (4)	0.017 (1)	0.0061 (5)	0.014 (4)	0.011 (2)	0.009 (1)
C(13)	0.367 (1)	0.1236 (8)	0.1795 (5)	0.024 (2)	0.0107 (7)	0.0050 (3)	0.003 (2)	0.013 (1)	0.0010 (8)
C(14)	0.321 (2)	0.044 (1)	0.2416 (6)	0.031 (3)	0.015 (1)	0.0051 (4)	0.001 (3)	0.016 (2)	0.001 (1)
C(15)	0.492 (1)	0.2746 (7)	0.0411 (5)	0.017 (2)	0.0096 (6)	0.0046 (3)	0.006 (2)	0.009 (1)	0.0012 (7)
C(16)	0.428 (2)	0.305 (1)	0.1221 (7)	0.031 (3)	0.017 (1)	0.0063 (5)	0.005 (3)	0.014 (2)	0.0008 (1)
C(17)	0.303 (2)	0.4099 (8)	0.0490 (7)	0.024 (3)	0.0083 (6)	0.0084 (5)	0.014 (2)	0.016 (2)	0.005 (1)
C(18)	0.199 (3)	0.481 (1)	0.014 (2)	0.037 (5)	0.011 (1)	0.016 (2)	0.002 (3)	0.020 (4)	0.002 (2)
C(19)	0.201 (1)	0.0047 (7)	0.1522 (5)	0.013 (2)	0.0098 (6)	0.0044 (3)	0.003 (2)	0.007 (1)	0.0016 (6)
C(20)	0.147 (1)	0.1865 (7)	0.0883 (4)	0.019 (2)	0.0092 (6)	0.0039 (2)	0.004 (1)	0.012 (1)	0.0008 (6)
O(1)	0.233 (1)	0.0288 (8)	0.2124 (3)	0.041 (2)	0.0173 (9)	0.0031 (2)	0.013 (2)	0.008 (1)	0.0022 (6)
O(2)	0.144 (1)	0.2734 (6)	0.1088 (5)	0.043 (2)	0.0081 (4)	0.0064 (3)	0.003 (2)	0.018 (1)	0.0050 (6)

	$x/a$	$y/b$	$z/c$	$B$ ( $\text{\AA}^2$ )		$x/a$	$y/b$	$z/c$	$B$ ( $\text{\AA}^2$ )
H(5)	0.434	0.049	0.079	4.0	H(143)	0.396	0.035	0.270	6.0
H(10)	0.084	0.318	0.106	4.0	H(151)	0.576	0.216	0.035	5.0
H(111)	0.200	0.329	0.209	5.0	H(152)	0.546	0.341	0.012	5.0
H(112)	0.078	0.375	0.167	5.0	H(161)	0.505	0.333	0.145	6.0
H(121)	0.062	0.348	0.294	6.0	H(162)	0.369	0.239	0.152	6.0
H(122)	0.127	0.266	0.242	6.0	H(163)	0.339	0.364	0.129	6.0
H(123)	0.005	0.220	0.284	6.0	H(171)	0.419	0.433	0.063	5.0
H(131)	0.391	0.198	0.200	5.0	H(172)	0.268	0.422	0.094	5.0
H(132)	0.484	0.099	0.145	5.0	H(181)	0.234	0.470	0.060	6.0
H(141)	0.213	0.068	0.276	6.0	H(182)	0.083	0.459	0.028	6.0
H(142)	0.306	0.031	0.221	6.0	H(183)	0.209	0.562	0.002	6.0

Table 3. Bond distances and angles with *e.s.d.*'s in parentheses

Rh—N(1)	2.079 (7) Å	Rh—N(1)—C(1)	130.6 (6)°
Rh—N(2)	2.088 (7)	Rh—N(2)—C(9)	129.2 (6)
Rh—C(19)	1.850 (10)	Rh—N(1)—C(4)	117.0 (6)
Rh—C(20)	1.854 (11)	Rh—N(2)—C(6)	117.8 (5)
C(19)—O(1)	1.133 (15)	C(1)—N(1)—C(4)	107.7 (7)
C(20)—O(2)	1.129 (15)	C(6)—N(2)—C(9)	108.3 (7)
N(1)—C(1)	1.359 (12)	N(1)—C(1)—C(2)	109.1 (8)
N(1)—C(4)	1.378 (11)	N(1)—C(4)—C(3)	109.1 (7)
N(2)—C(6)	1.351 (11)	N(2)—C(6)—C(7)	109.0 (7)
N(2)—C(9)	1.371 (12)	N(2)—C(9)—C(8)	108.6 (8)
C(1)—C(2)	1.442 (14)	C(1)—C(2)—C(3)	107.8 (9)
C(3)—C(4)	1.451 (13)	C(4)—C(3)—C(2)	106.2 (8)
C(6)—C(7)	1.458 (12)	C(6)—C(7)—C(8)	106.4 (8)
C(8)—C(9)	1.438 (14)	C(9)—C(8)—C(7)	107.5 (9)
C(2)—C(3)	1.363 (14)	C(5)—C(4)—N(1)	125.9 (8)
C(7)—C(8)	1.361 (13)	C(5)—C(6)—N(2)	125.2 (8)
C(4)—C(5)	1.396 (12)	C'(10)—C(1)—N(1)	126.4 (9)
C(5)—C(6)	1.401 (12)	C(10)—C(9)—N(2)	126.7 (9)
C(1)—C'(10)	1.385 (14)	C(5)—C(4)—C(3)	125.0 (8)
C(9)—C(10)	1.422 (14)	C(5)—C(6)—C(7)	125.7 (8)
C(2)—C(11)	1.496 (17)	C'(10)—C(1)—C(2)	124.4 (9)
C(3)—C(13)	1.501 (16)	C(10)—C(9)—C(8)	124.6 (9)
C(7)—C(15)	1.497 (14)	C(4)—C(5)—C(6)	123.2 (8)
C(8)—C(17)	1.508 (17)	C(9)—C(10)—C'(1)	131.2 (10)
C(11)—C(12)	1.439 (22)	C(1)—C(2)—C(11)	125.0 (10)
C(13)—C(14)	1.488 (20)	C(4)—C(3)—C(13)	124.0 (9)
C(15)—C(16)	1.513 (20)	C(6)—C(7)—C(15)	124.9 (8)
C(17)—C(18)	1.521 (34)	C(9)—C(8)—C(17)	125.3 (10)
		C(3)—C(2)—C(11)	127.0 (10)
N(1)—Rh—N(2)	84.9 (3)°	C(2)—C(3)—C(13)	129.8 (10)
N(1)—Rh—C(20)	92.7 (4)	C(8)—C(7)—C(15)	128.7 (9)
N(2)—Rh—C(19)	92.8 (4)	C(7)—C(8)—C(17)	127.1 (10)
C(19)—Rh—C(20)	89.0 (5)	C(2)—C(11)—C(12)	113.6 (12)
N(1)—Rh—C(19)	173.7 (4)	C(3)—C(13)—C(14)	114.4 (11)
N(2)—Rh—C(20)	173.4 (4)	C(7)—C(15)—C(16)	114.7 (10)
Rh—C(19)—O(1)	175.9 (10)	C(8)—C(17)—C(18)	111.8 (15)
Rh—C(20)—O(2)	178.6 (10)		

was terminated when no significant changes in parameters were observed. The final values of  $R$  and  $R_w$ , where  $R_w = [\sum w\Delta^2 / \sum w|F_o|^2]^{1/2}$ , were 0.060 and 0.068, respectively.

The atomic scattering factors were taken as those of the neutral atoms given in *International Tables for X-ray Crystallography* (1962). The final positional and thermal parameters are given in Table 2. Bond distances and angles involving non-hydrogen atoms are given in Table 3.\* A stereoscopic view of the molecule together with the numbering of the atoms is shown in Fig. 1, where primed atoms are related by the centre of symmetry to their non-primed equivalents. Fig. 2 shows the crystal structure. Deviations of the atoms from the least-squares planes are given in Table 4.

The calculations were carried out on a HITAC 8700 in Tokyo Institute of Technology and on a HITAC 8800 in the University of Tokyo, with the programs in the *Universal Crystallographic Computation Program System* (1967) and with programs developed by the

\* A table of observed and calculated structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30594 (10 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

two of the authors (A.T. and Y.S.): *TLSU* for the determination of the cell dimensions, *TDRW* for the

Table 4. Least-squares planes

Plane (1):	$0.9616X + 0.1490Y + 0.2305Z = 1.418$
Plane (2):	$0.1903X + 0.4418Y + 0.8767Z = 0$
Plane (3):	$0.4688X + 0.5390Y + 0.6998Z = 0.651$
Plane (4):	$0.4575X + 0.2592Y + 0.8506Z = 0.620$

$X$ ,  $Y$  and  $Z$  are in Å along the  $a$ ,  $b$  and  $c^*$  axes respectively. Starred atoms are used to define the plane.

Plane (1)		Plane (2)	
Atom	Deviation	Atom	Deviation
N(1)*	-0.002 Å	N(1)*	0 Å
N(2)*	0.002	N(2)*	0
C(19)*	-0.003	N'(1)*	0
C(20)*	0.003	N'(2)*	0
Rh	-0.105	Rh	1.322

Plane (3)		Plane (4)	
Atom	Deviation	Atom	Deviation
C(1)*	-0.002 Å	C(6)*	-0.001 Å
C(2)*	0.003	C(7)*	0.001
C(3)*	-0.003	C(8)*	-0.001
C(4)*	0.002	C(9)*	0.001
N(1)	0.044	N(2)	0.049
Rh	0.883	Rh	0.856
C(5)	-0.095	C(5)	-0.139
C'(10)	-0.111	C(10)	-0.112
C(11)	-0.075	C(15)	-0.026
C(13)	-0.047	C(17)	-0.079

data reduction, *TAWS* for the weighting-scheme analyses, and *DCMS* for the stereoscopic-pair drawing.

### Discussion

As shown in Fig. 1, the metalloporphyrin is centrosymmetric and the two Rh(I) atoms are bonded to the porphyrin, one above and the other below the macrocyclic plane. These features are similar to those of the Re(I) complex (Cullen, Meyer, Srivastava & Tsutsui, 1972). Each Rh atom, however, has square-planar coordination: the nearest neighbours to a Rh are two nitrogen atoms in adjacent pyrroles of the macrocycle and two carbon atoms of the carbonyls, and these four are coplanar within 0.003 Å (Table 4). This is the first known example of a metalloporphyrin system in which two monovalent metal atoms have square-planar coordination.

Displacement of a metal atom from the plane containing the four nitrogen atoms, 1.322 Å, is smaller by 0.1 Å than that in the Re(I) complex. The average Rh–N distance, 2.084 Å, is somewhat longer than that of 2.038 Å found in bis(dimethylamino)etio(I)porphinatorhodium(III) chloride dihydrate, in which the Rh(III) atom lies at the centre of the porphinato core (Hanson, Gouterman & Hanson, 1973). The carbonyl molecules are linearly bonded to the metal atoms at a distance of 1.85 Å, which is comparable with that in  $\mu$ -dichlorobis[dicarbonylrhodium(I)] (Dahl, Martell & Wampler, 1961).

As shown in Fig. 3, the Rh atom deviates by 0.105 Å from the basal plane of the coordinated atoms toward the mid-point of N'(1) and N'(2) which are bonded to the other Rh', so that Rh...N'(1) and Rh...N'(2) are 3.062 and 3.086 Å, respectively. The nearest intermolecular approach of H(5) to Rh, 3.5 Å, is not close

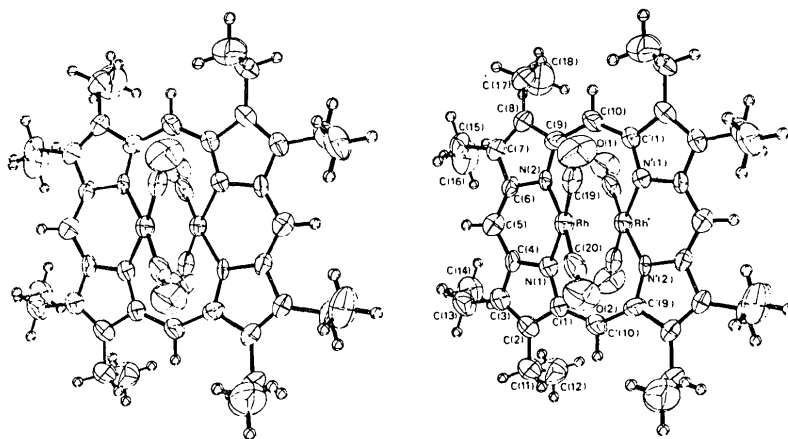


Fig. 1. Stereoscopic drawing of the molecule of  $\mu$ -1,2,3,4,5,6,7,8-octaethylporphinatobis[dicarbonylrhodium(I)]. The non-hydrogen atoms are represented by their thermal ellipsoids scaled to include 50% probability, while the hydrogen atoms are represented by spheres of arbitrary size.

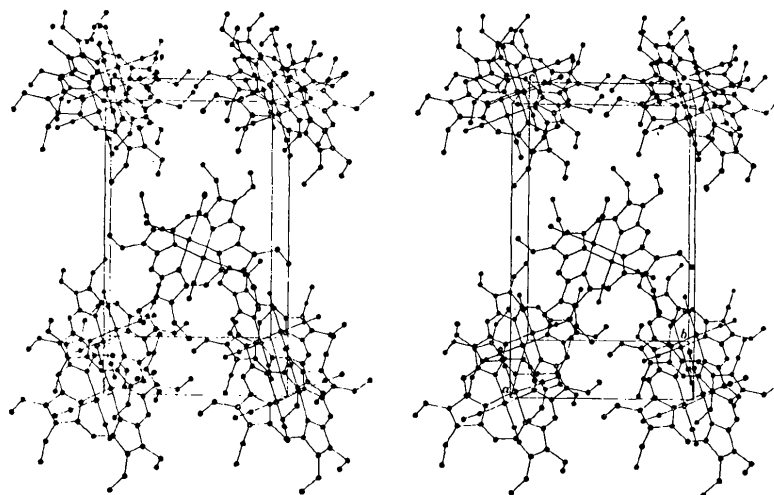


Fig. 2. Stereoscopic diagram showing the molecular packing in the unit cell viewed along the  $a^*$  axis.

enough to cause the deviation of Rh. The Rh' atom is located at a distance of 3.094 Å from Rh, in a direction tilted by 31.9° from the normal to the basal plane. This distance is considerably longer than the Rh(I)–Rh(I) single bond (2.617 to 2.705 Å) which is found in several cyclopentadienyl–carbonyl–rhodium(I) complexes (Mills & Nice, 1967; Mills & Paulus, 1967; Paulus, 1969). The Rh deviation, therefore, is attributed to a 'secondary interaction' of Rh with the lone pairs of N'(1) and N'(2); the tetrahedral configurations around N'(1) and N'(2) are favourable to this interaction. If these nitrogens are regarded as the two participants in the ligand field around Rh, the coordination is formally a trigonal prism. However, the metal–metal interaction cannot be ruled out until the diamagnetism of this complex is observed.\* In any case, the 'secondary interaction' is not so strong, inasmuch as the deviation of Rh is much smaller than that of the typical square-pyramidal coordination in high-spin ferric porphyrins (Koenig, 1965; Hoard, Hamor, Hamor & Caughey, 1965; Hoffman, Collins, Day, Fleischer, Srivastava & Hoard, 1972) and in zinc(II) porphyrins (Collins & Hoard, 1970; Spaulding, Eller, Bertrand & Felton, 1974).

The C(19) to C'(1), C(10), and C(9) distances (3.18, 3.26 and 3.22 Å) and the C(20) to C'(9), C'(10), and C(1) distances (3.18, 3.24, and 3.22 Å) in the molecule are significantly shorter than twice the van der Waals radius of aromatic carbon. These close approaches support the 'secondary interaction' described above.

The porphyrin macrocycle is considerably deformed. The two pyrrole rings bonded to one Rh atom are inclined upward from the macrocyclic plane and the other two downward, so that the planes of the adjacent

pyrroles (Table 4) make an angle of 18.3°. The two nitrogen atoms, N(1) and N(2), are deviated significantly by 0.044 and 0.049 Å from each pyrrole plane to form an envelope conformation. In both rings, these deviations occur on the same side as Rh, while the two methine and the two ethyl carbon atoms are all on the opposite side. These deformation features are contrary to those in the Re(I) complex with octahedral coordination (Cullen, Meyer, Srivastava & Tsutsui, 1972).

The average values of the chemically equivalent bond distances and angles in the porphyrin macrocycle are: N–C<sub>α</sub> 1.36<sub>5</sub>, C<sub>α</sub>–C<sub>β</sub> 1.44<sub>7</sub>, C<sub>α</sub>–C<sub>m</sub> 1.40<sub>1</sub>, C<sub>β</sub>–C<sub>β</sub> 1.36<sub>2</sub> Å, C<sub>α</sub>–N–C<sub>α</sub> 108.0, N–C<sub>α</sub>–C<sub>β</sub> 109.0, C<sub>α</sub>–C<sub>β</sub>–C<sub>β</sub> 107.0, C<sub>m</sub>–C<sub>α</sub>–N 126.1, and C<sub>m</sub>–C<sub>α</sub>–C<sub>β</sub> 124.9°, where C<sub>α</sub>, C<sub>β</sub> and C<sub>m</sub> are α- and β-carbons in pyrrole, and methine carbon, respectively. These are similar to those found in the usual metalloporphyrins despite the deformed structure. Closer examination shows that the deformation of porphyrin results in a marked asymmetry in bond angles. The two C<sub>α</sub>–C<sub>m</sub>–C<sub>α</sub> angles at C(5) and C(10) differ by 8.0° and the latter angle, C(9)–C(10)–C'(1) 131.2°, is the largest among those in many other metalloporphyrins. The chelation of the two pyrrole rings with the same Rh atom contracts the bond angle at C(5) which links them. On the other hand, the large angle at C(10) is plausible if C(10) and C'(10) are regarded as joints of the two metal chelates. The Rh–N bonds do not bisect the C<sub>α</sub>–N–C<sub>α</sub> angle; the average difference in the Rh–N–C<sub>α</sub> angles reaches 12°. The N–C<sub>α</sub> bond distance is significantly shorter than the 1.42 Å involving the bridge nitrogen atom of the octahedral Re(I) complex (Cullen, Meyer, Srivastava & Tsutsui, 1972).

All the terminal C–C bonds in the ethyl groups are apparently shortened from the normal value because of the large thermal motion.

As shown in Fig. 2, the C(5) atom comes into contact with the C'(5) atom in the neighbouring molecule along the *a* axis, at a distance of 3.15 Å in a direction almost perpendicular to the macrocyclic plane. Thus the molecules are stacked through the overlapping of the aromatic methine groups. Except for this contact, the molecules are packed by van der Waals interactions, mainly between the carbonyl oxygen atoms and the peripheral ethyl groups. The configurations of the ethyl groups are similar to those observed in the free base (Lauher & Ibers, 1973) and the tin(IV) complex (Cullen & Meyer, 1973), but different from those in the nickel(II), the low-spin iron(III) complexes (Meyer, 1972; Takenaka, Sasada, Watanabe, Ogoshi & Yoshida, 1972), and the monocationic species (Hirayama, Takenaka, Sasada, Watanabe, Ogoshi & Yoshida, 1974*a, b*).

The present metalloporphyrin is obtained by carefully controlled reaction of the free base and μ-dichlorobis[dicarbonylrhodium(I)] in benzene solution (Yoshida, Ogoshi, Omura, Watanabe & Kurosaki, 1972). This complex is stable to air in the crystalline state but oxidized in refluxing chloroform to the trivalent rho-

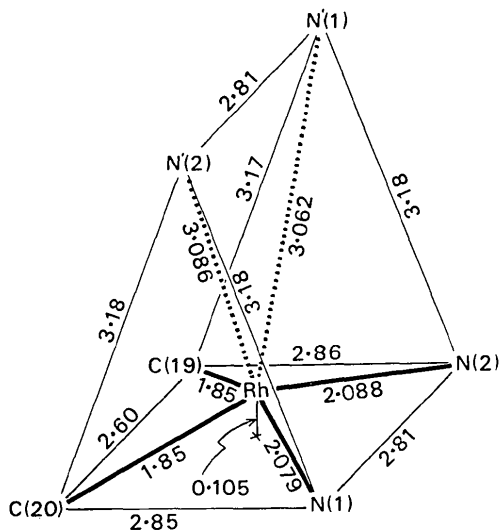


Fig. 3. Geometry about the Rh atom.\*Distances are in Å.

\* The present Rh···Rh' distance is shorter than that found in [Rh(CO)<sub>2</sub>Cl]<sub>2</sub> (Dahl, Martell & Wampler, 1961).

dium complex in which the ratio of metal to porphyrin is 1. In this process, one of the two metal atoms should migrate to the centre of the porphyrin, as observed in the structure of bis(dimethylamino)etio(I)porphyrinorhodium(III) chloride dihydrate (Hanson, Gouterman & Hanson, 1973). Therefore the present complex can be regarded as an intermediate of the reaction involving the oxidation of the monovalent metal.

The mechanism of metal bonding to porphyrin has been investigated by many authors (Choi & Fleischer, 1963; Brisbin & Balahura, 1968; Weaver & Hambright, 1969; Kingham & Brisbin, 1970; Hambright & Fleischer, 1970; Burham & Zuckerman, 1970; James & Hambright, 1973; Baker, Hambright & Wagner, 1973). In the displacement mechanism (Phillips, 1963; Falk, 1964) the metal ion first forms an activated complex with porphyrin in which the macrocycle is deformed, and the protons are then displaced from the nitrogen atoms by the metal. An upper moiety of the present structure suggests a model of such an intermediate where the metal is incorporated with square-planar coordination. Although Khosropour & Hambright (1972) have supposed that the metal ion first binds to the two pyrroline-type nitrogen atoms which are situated diagonally through the centre of porphyrin, the distance between them seems to be too long for square-planar coordination. Consequently, the two adjacent nitrogen atoms are likely to bind with the metal atom and this might interact secondarily with the remaining two nitrogen atoms, as mentioned above. In a similar way, the structure of the Re(I) complex (Cullen, Meyer, Srivastava & Tsutsui, 1972) can be applicable to a model for incorporation of the metal with octahedral coordination.

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#### References

- BAKER, H., HAMBRIGHT, P. & WAGNER, L. (1973). *J. Amer. Chem. Soc.* **95**, 5942-5946.
- BRISBIN, D. A. & BALAHURA, R. J. (1968). *Canad. J. Chem.* **46**, 3431-3436.
- BURNHAM, B. F. & ZUCKERMAN, J. J. (1970). *J. Amer. Chem. Soc.* **92**, 1547-1550.
- CHOI, E. I. & FLEISCHER, E. B. (1963). *Inorg. Chem.* **2**, 94-97.
- COLLINS, D. M. & HOARD, J. L. (1970). *J. Amer. Chem. Soc.* **92**, 3761-3771.
- COLLINS, D. M., SCHEIDT, W. R. & HOARD, J. L. (1972). *J. Amer. Chem. Soc.* **94**, 6689-6696.
- CULLEN, D. L. & MEYER, E. F. JR (1973). *Acta Cryst.* **B29**, 2507-2515.
- CULLEN, D., MEYER, E., SRIVASTAVA, T. S. & TSUTSUI, M. (1972). *J. Amer. Chem. Soc.* **94**, 7603-7605.
- DAHL, L. F., MARTELL, C. & WAMPLER, D. L. (1961). *J. Amer. Chem. Soc.* **83**, 1761-1762.
- FALK, J. E. (1964). In *Porphyryns and Metalloporphyryns*. Amsterdam: Elsevier.
- HAMBRIGHT, P. & FLEISCHER, E. B. (1970). *Inorg. Chem.* **9**, 1757-1761.
- HANSON, L. K., GOUTERMAN, M. & HANSON, J. C. (1973). *J. Amer. Chem. Soc.* **95**, 4822-4829.
- HIRAYAMA, N., TAKENAKA, A., SASADA, Y., WATANABE, E., OGOSHI, H. & YOSHIDA, Z. (1974a). *Chem. Commun.* pp. 330-331.
- HIRAYAMA, N., TAKENAKA, A., SASADA, Y., WATANABE, E., OGOSHI, H. & YOSHIDA, Z. (1974b). To be published.
- HOARD, J. L. (1971). *Science*, **174**, 1295-1302.
- HOARD, J. L., HAMOR, M. J., HAMOR, T. A. & CAUGHEY, W. S. (1965). *J. Amer. Chem. Soc.* **87**, 2312-2319.
- HOFFMAN, A. B., COLLINS, D. M., DAY, V. W., FLEISCHER, E. B., SRIVASTAVA, T. S. & HOARD, J. L. (1972). *J. Amer. Chem. Soc.* **94**, 3620-3626.
- International Tables for X-ray Crystallography* (1962). Vol. III, pp. 201-245. Birmingham: Kynoch Press.
- IZUMI, T. (1971). *Jap. J. Appl. Phys.* **10**, 1724-1728.
- JAMES, J. & HAMBRIGHT, P. (1973). *Inorg. Chem.* **12**, 474-476.
- KHOSROPOUR, R. & HAMBRIGHT, P. (1972). *Chem. Commun.* pp. 13-14.
- KINGHAM, D. J. & BRISBIN, D. A. (1970). *Inorg. Chem.* **9**, 2034-2037.
- KOENIG, D. F. (1965). *Acta Cryst.* **18**, 663-673.
- LAUHER, J. W. & IBERS, J. A. (1973). *J. Amer. Chem. Soc.* **95**, 5148-5152.
- MEYER, E. F. JR (1972). *Acta Cryst.* **B28**, 2162-2167.
- MILLS, O. S. & NICE, J. P. (1967). *J. Organometal. Chem.* **10**, 337-342.
- MILLS, O. S. & PAULUS, E. F. (1967). *J. Organometal. Chem.* **10**, 331-336.
- PAULUS, E. F. (1969). *Acta Cryst.* **B25**, 2206-2213.
- PHILLIPS, J. N. (1963). In *Comprehensive Biochemistry*. Vol. 9, pp. 34-72, edited by M. FLORKIN and E. H. STOTZ. Amsterdam: Elsevier.
- SPAUDLING, L. D., ELLER, P. G., BERTRAND, J. A. & FELTON, R. H. (1974). *J. Amer. Chem. Soc.* **96**, 982-987.
- SHIMANOUCI, H., IBATA, K. & SASADA, Y. (1971). Unpublished work.
- STONE, A. & FLEISCHER, E. B. (1968). *J. Amer. Chem. Soc.* **90**, 2735-2748.
- TAKENAKA, A. & SASADA, Y. (1973). Presented at the Annual Meeting Cryst. Soc. Japan, Osaka, Japan. *Abstracts*, p. 27.
- TAKENAKA, A., SASADA, Y., OMURA, T., OGOSHI, H. & YOSHIDA, Z. (1973). *Chem. Commun.* pp. 792-793.
- TAKENAKA, A., SASADA, Y., WATANABE, E., OGOSHI, H. & YOSHIDA, Z. (1972). *Chem. Lett.* pp. 1235-1238.
- Universal Crystallographic Computation Program System* (1967). Edited by T. SAKURAI, Crystallographic Society of Japan.
- WEAVER, J. & HAMBRIGHT, P. (1969). *Inorg. Chem.* **8**, 167-168.
- WILSON, A. J. C. (1942). *Nature, Lond.* **150**, 151-152.
- YOSHIDA, Z., OGOSHI, H., OMURA, T., WATANABE, E. & KUROSAKI, T. (1972). *Tetrahedron Lett.* pp. 1077-1080.